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Precursor Derived SiC-Carbon Nanotube Composites

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Abstract

Nanocomposites of SiC ceramic and carbon nanotubes were prepared. Surface modified carbon nanotubes and nanofibers were mixed with a silicon carbide polymer precursor material, allylhydridopolycarbosilane, using high energy sonication followed by crosslinking and pyrolysis. Samples were examined using electron microscopy and tests were performed to investigate the crack inhibiting effects of the nano-reinforcements on the silicon carbide.

Keywords

Carbon Nanotube, Silicon Carbide, Nanocomposite

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Introduction

Since the published work of Iijima in 1991 [1] there has been considerable interest and research into the structure and properties of carbon nanotubes and the effect of adding these fullerene molecules into various other material systems. Carbon nanotubes have very unique properties such as very high strength, modulus, high thermal conductivity, flexibility and electrical properties such as field-emission and chirality dependent electrical conductivity. Carbon nanotubes have been reported to have an elastic modulus of 1.5 TPa [2] and a tensile strength on the order of 50 GPa. With these properties, carbon nanotubes could be ideal reinforcing agents in matrix materials such as polymers and ceramics. Van der Waals attraction, high aspect ratios and high surface area lead to significant agglomeration of the nanotubes. In order to create composites where the properties of the nanotubes are realized, the bundles and agglomerations must be broken up and the nanotubes dispersed throughout the matrix.

Polymer materials have seen increases in strength, electrical conductivity, strain to failure, and damping properties [3-5]. Research on ceramic materials has seen mixed results with some reporting modest improvement in properties and some showing a degradation of properties. Zhan et al. have shown a three-fold increase in fracture toughness of nanocrystalline alumina produced by spark plasma sintering with the addition 10 vol% of single-walled carbon nanotubes [6]. Siegal et al., reported a 24% increase in fracture toughness of alumina with 10 vol% multi-walled carbon nanotubes [3]. In the study of a silicon carbide ceramic, Ma et al. show only a 10% increase in fracture toughness of MWNT reinforced nano-SiC [7]. Meanwhile, Wang et al. report an increase in contact damage resistance for the ceramic/nanotube composites but not the fracture toughness as measured by indentation testing [8]. Some have begun to look at dispersing nanotube fillers into preceramic polymers [9, 10]. Katsuda et al. saw a 60% increase in fracture toughness investigated by a thermal loading technique for a Si-C-N material with 2 wt% multi-walled nanotubes (MWNT).

Composites formed by conventional powder based processing methods must overcome the

difficulty in dispersing the nanotubes in the powder media and achieving adequate interfacial bonding between the nanotube and the ceramic matrix. In addition, damage to the nanotube may occur at the very high processing temperatures. In contrast, a liquid preceramic polymer provides an ideal situation for dispersing nanotubes and nanofibers and is followed by lower processing temperatures.

Experimental

Multi-walled carbon nanotubes (MWNT) and carbon nanofibers (CNF) were investigated in order to determine nanofiller size effects on the microstructure and crack inhibiting behavior. Both the MWNTs and the CNFs were in the oxidized form when purchased from Cheap Tubes, Inc (Brattleboro, VT, USA) and Applied Sciences (Cedarville, OH, USA), respectively. The MWNT had an average diameter of 10-20nm and average length of 50 μ m. The average diameter of the CNF was 100-200nm and a length between 30-100 μ m.

Allylhydridopolycarbosilane, a commercial silicon carbide polymer precursor material, was provided by Starfire Systems (Malta, NY, USA). Silicon carbide powder was used as filler in the composite materials to reduce the amount of shrinkage as the materials converts from liquid precursor (0.998g/cc) to amorphous silicon carbide (2.45g/cc). The silicon carbide powder used was 700nm diameter UF-10 (H.C. Starck, USA) alpha silicon carbide. For a typical sample, the carbon nanotubes or carbon nanofibers and silicon carbide powder were mixed by stirring with the liquid polymer precursor followed by 30 minutes of bath sonication and 3 minutes of pulsed high energy sonication using a Cole Parmer 750-Watt Ultrasonic Processor. Samples were then heat treated in an inert atmosphere for cross-linking and pyrolysis. Samples were slowly heated to 250°C and held for 1hr followed by continued slow heating to 450°C and another hold for 1hr. Samples were further heated to 850°C and held for 1hr and then slowly cooled to room temperature. The microstructures of the composites were examined using a JEOL 840-A SEM and a Perkin-Elmer PHI 600 Scanning Auger Microprobe. Vickers indentations were made using 1kg of force on the CNF samples in order to study crack formation.

Results and Discussion

Scanning electron microscopy of the material was performed in order to examine the microstructure. The items of interest in the microstructural examination were the dispersion of the CNF/MWNT, the nature of the interface between the nano-reinforcement and the matrix and a qualitative look at crack initiation from Vickers indentation. Figure 1 shows SEM of MWNT and CNF mixed with the SiC powder. The nanofibers are about an order of magnitude larger than the nanotubes.

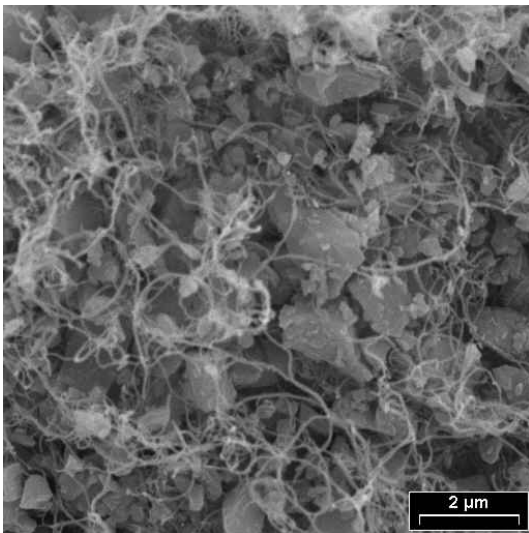


Fig. 1a. MWNT and SiC powder.

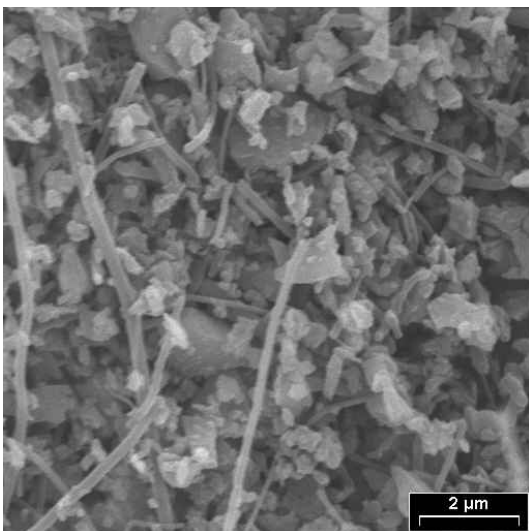


Fig. 1b. CNF and SiC powder.

Fig. 2 shows a fracture surface of a 5wt% CNF sample. In this micrograph, it appears that the ceramic formed from the precursor material has bonded well to the carbon nanofibers. This can be seen in the region marked "A" where ceramic material has been chipped away from the surface but is still attached to the nanofiber indicating a strong bond between the two. In the region marked "B" a hole can be seen where a nanofiber has pulled out from the matrix or has broken. This is a good indication that the nanofibers could act as good strengthening additives during mechanical testing. If there is a strong interface between the nanofiber and the matrix then there should be large energy dissipation in fiber pull-out. Similar examples of the phenomena marked A and B are seen in other places throughout the micrograph. A high magnification micrograph of a nanofiber is seen in Fig.3. Although not conclusive, it appears there may be a thin film of ceramic coating the nanofiber. In order to investigate this further, the scanning Auger microprobe was used to perform mapping and line scans to detect Si, C and O.

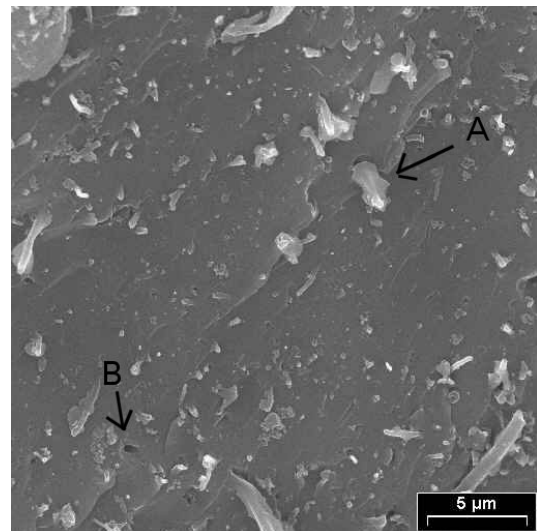


Fig. 2. Fracture surface of 5wt% CNF sample

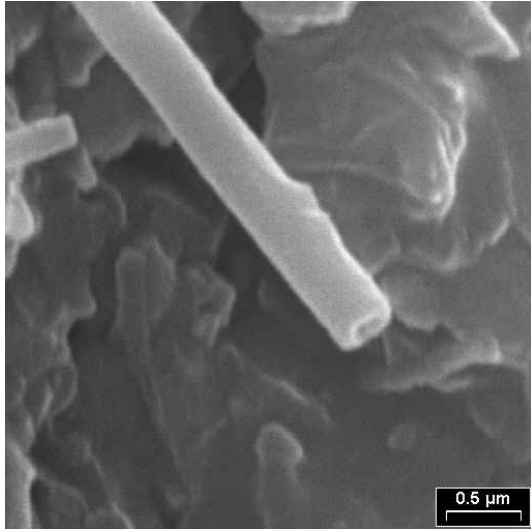


Fig. 3. Carbon nanofiber with possible ceramic coating.

The Auger line scans were performed over an area with several nanofibers extending from a fracture surface as seen in Fig.4. When the line scan passes over a nanofiber, the carbon content and the oxygen content rise. This is due to the carbon structure of the nanofiber and the oxygen present in the functional groups attached during oxidation. The Si peaks are low and during this point in the study it is inconclusive to verify by elemental analysis whether a SiC coating exists on the nanofiber. Additional Auger studies are currently being conducted.

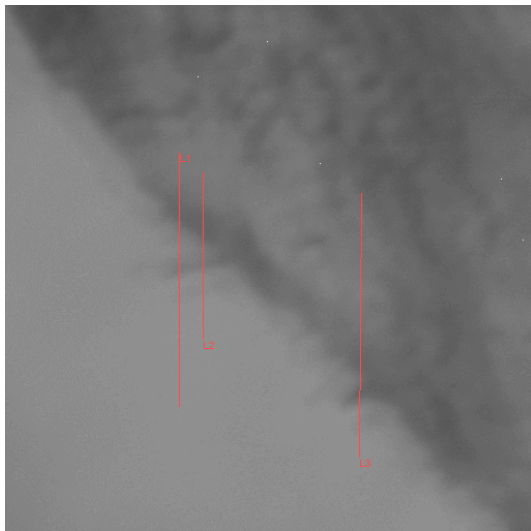


Fig. 4. Scanning Auger Microprobe line scans over CNF (the length of each side of the micrograph is 50 microns).

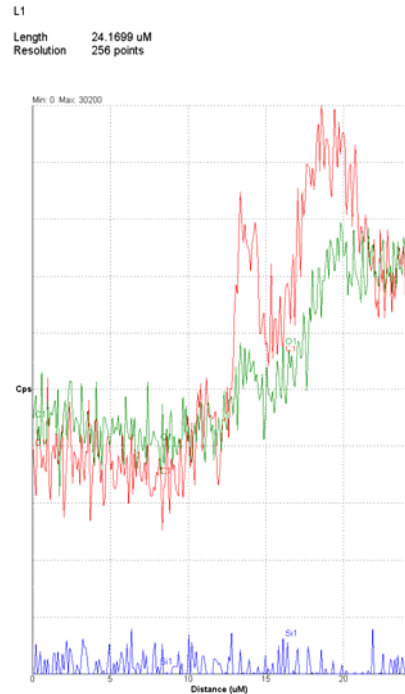


Fig. 5. Elemental linescan analysis. Top line- Carbon, middle line-Oxygen, bottom line-Silicon

Vickers indentation showed that samples containing the carbon nanofibers were less likely to form cracks at the corners of the indents than the samples containing no nanofibers. The samples containing 0wt% nanofibers had 100% more cracks propagating from the indent corners than those samples which did contain nanofibers. Figures 6 and 7 show a 5wt% CNF sample containing no cracks and a sample with no nanofibers containing a large crack propagating from the corner of the Vickers indent. Fig 8 shows nanofibers bridging cracks in the silicon carbide, a method of strengthening in composite materials.

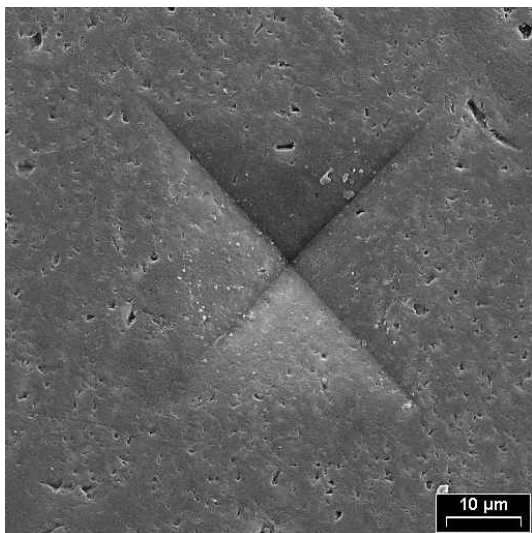


Fig. 6. Vickers indent of a 5wt% CNF sample showing no cracks propagating from the indent corners.

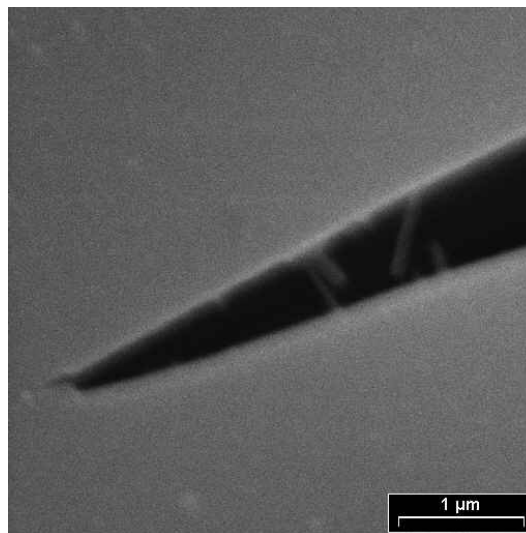


Fig. 8. Carbon nanofibers seen bridging a crack near the tip

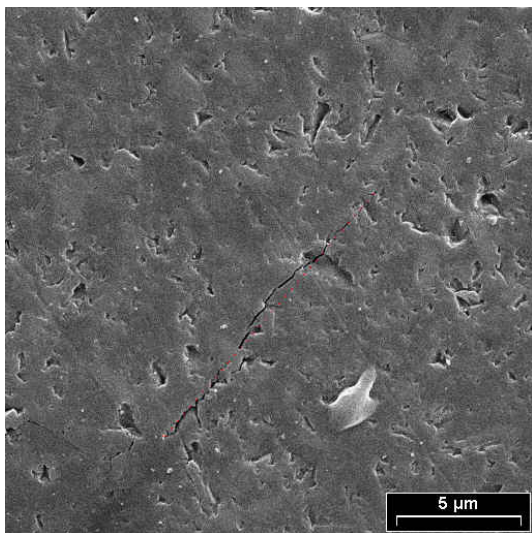


Fig. 7. Sample containing no CNF showing crack propagating from Vickers indent.

MWNT samples were made and observed under the SEM. Vickers indentation testing was not performed on the samples because adequate dispersion has not been achieved. Due to the high surface area of the nanotubes, it is difficult to achieve a high loading of nanotubes without completely absorbing the polymer precursor. Current studies are focusing on using solvent methods to first disperse the nanotubes in the precursor material prior to evaporating the solvent and pyrolyzing.

Summary

A unique method of using a silicon carbide precursor material and carbon nanotubes and nanofibers to make nanocomposites has been performed. Electron microscopy was used to examine microstructures and to show that the polymer material bonds to the nanofibers which could result in strengthening of the silicon carbide and decreased crack propagation. Further studies are being performed in order to evaluate the crack inhibiting effects of the MWNT and to further examine the chemistry of the nanofiber surface.

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